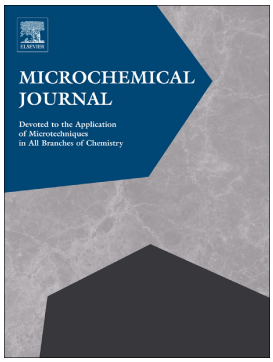

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PII: S0026-265X(18)30310-2
DOI: doi:10.1016/j.microc.2018.05.043
Reference: MICROC 3192

To appear in: *Microchemical Journal*

Received date: 14 March 2018
Revised date: 7 May 2018
Accepted date: 24 May 2018

Please cite this article as: Laura Fernández, Martín Fernández Baldo, Germán Messina, Franco A. Bertolino, Julio Raba, Pedro R. Aranda , Graphene-based materials as solid phase extraction sorbent for chromium(VI) determination in red wine. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Microc(2017), doi:10.1016/j.microc.2018.05.043

Graphene-based materials as solid phase extraction sorbent for Chromium (VI) determination in red wine

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ABSTRACT

We report a novel and selective method for the preconcentration and determination of Cr(VI) in red wine through their adsorption on a tertiary amine, ALIQUAT 336, a commercial anionic exchanger extractant, widely used for the selective extraction of Cr(VI) over Cr(III). The determinations were made directly on the solid, by X-ray fluorescence spectrometry, method and large areas held by the graphene, making them a promising solid sorbent for preconcentration procedures, direct quantification of the analyte in the solid sorbent; there by reducing the number of reagents used thus minimizing handling of the sample. A high preconcentration factor was achieved for a very low volume of sample. The enrichment factor was calculated after considering that the thin film obtained from the 10 mL solution of 1 mg L^{-1} of Cr(VI) has a real thickness of 0.04 mm and a final diameter of 16.7 mm, so that the volume deposited on the pellet was 0.0088 cm^3 and the preconcentration factor can be calculated to be 10^4.

Keywords: Graphene, Red wine, Chromium; ALIQUAT 336; Thin film; X-ray fluorescence.

Introduction

Wine has been consumed worldwide since time immemorial. Argentine plays an important role in international wine production. In addition, the wine consumption in this country is of considerable relevance to the national economy. The current wine consumption is above 4568×10^5 L per year according to the National Institute of Statistics [1]. High quality wines are produced in Argentine, some of them being recognized worldwide [2–4].

Wine is an extraordinarily complex chemical matrix being composed of alcohol, water, sugar, organic compounds and inorganic compounds. The ions present in high concentrations are K, Ca, Na and Mg. Other elements also are present in trace concentrations, such as Se, Pb and Cr [5–8]. Some trace elements usually are used as active agents in herbicides and pesticides for vineyard treatment [9], but the bioaccumulation in grapes and wines also comes from environmental pollution, equipment used in winery and production methods performed from vineyard to bottling [10–14].

On the basis of the analysis of chromium concentrations for different vintage wines of the same vineyard and winery [15] found that Cr content significantly increased with the age of the wine. This could be the result of contamination during storage by stainless steel or after bottling by chromium oxides used for pigmentation of the bottle during the aging process [16].

Chromium species exist in the environment mainly in two oxidation states, Cr(III) and Cr(VI), which have contrasting physiological effects. Trivalent chromium is essential to normal carbohydrate, lipid, and protein metabolism. In contrast, chromium(VI) can induce carcinogenesis because of its ability to cross biological membranes easily and react with protein components and nucleic acids inside the cell [17, 18]. For this reason, it is necessary to use a sensitive method for the determination of Cr(III) and Cr(VI) in different type samples. Also, the continuous monitoring of Cr(VI) in environmental and biological systems is of considerable relevance due to its elevated mobility in subsurface environments and bioaccumulative and toxic effects on living organisms [19-21].

The direct determination of metal ions in complex matrices is limited due to their usually low concentrations and matrix interferences. In trace analysis, therefore, preconcentration and/or separation of analytes are necessary to improve sensitivity and selectivity of analysis [22-24].

Solid phase extraction (SPE) is one of the most commonly used procedure in analyte preconcentration as well as for removing impurities from samples. The possibility to use a broad range of sorbent materials, chelating reagents and eluents make this method very attractive for sample treatment. Moreover, SPE procedures can be easily implemented and controlled in flow systems to perform appropriate sample pretreatment. The mechanism of sorption depends on the nature of a given sorbent and may include simple adsorption, complexation or ion-exchange. The choice of solid material for enrichment should be based on the content of the analyte, sample matrix and technique used for final detection [25-27]. The choice of appropriate adsorbent in a SPE procedure is a critical factor to obtain full recovery and high enrichment factors [28-34]. In our research group, we have employed different adsorbent, for example; activated carbon and carbon nanotubes, but nowadays we are working with graphene [35-36].

Graphene as a new allotrope of carbon material was successfully applied as an adsorbent. Moreover, the surface functionality of these sorbents can be easily modified to achieve selective sample extraction. Considering the superior properties and high chemical stability of graphene, it thus may serve as a good adsorbent for SPE. Notably, graphene is usually considered to be non-polar and hydrophobic. Graphene oxide (GO), in contrast, contains much more polar moieties, such as hydroxy, expoxy, and carboxy groups, and thus has a more polar and hydrophilic character than graphene [37-40].

In our work, a novel method was developed for preconcentration and determination of Cr(VI) in red wine through their adsorption on a tertiary amine, ALIQUAT 336, a commercial anionic exchanger extractant widely used [40] for the selective extraction of Cr(VI) over Cr(III). The determinations were made directly on the solid, by means of X-ray fluorescence spectrometry. The choice of graphene, as a

solid sorbent, for the preconcentration procedures, allows the direct quantification of the analyte; as well as it reduces the number of reagents used, thus minimizing the manipulation of the sample. A high preconcentration factor was achieved for a very low volume of sample.

2. Experimental

2.1. Reagents and apparatus

Commercial Graphene dispersion 1 mg mL^{-1} in DMF**,** were obtained from Aldrich (Chemical Co., Milwauke, WI, USA, www.sigmaaldrich.com).

The extractant, Tricaprylmethylammonium chloride $CH_3N[(CH_2)_7CH_3]_3Cl$) (ALIQUAT 336) was purchased from Fluka (Switzerland www.sigmaaldrich.com). A 1000 mg L^{-1} Cr(VI) stock standard solution was prepared from 2.8290 g potassium dichromate ($K_2Cr_2O_7$), Merck (Darmstadt, Germany www.merck.de) dissolved in ultrapure water and diluted to a final volume of 1000 mL. Working standard solutions were prepared by stepwise dilution from this solution. Ultrapure water (18.1 MΩ cm) was obtained from Barnstead EASY pure RF water system (Iowa, USA).

All the reagents used were of analytical-reagent grade and the presence of chromium was not detected within the working range.

Measurements were performed with a Philips PW1400 X-ray Fluorescence Spectrometer. The Cr K_α line was used for measurements. The conditions were selected appropriately. The pH of the solutions was measured using an Orion 701-A pH meter with an Ag/AgCl electrode. A M-23 Digital Orbital shaker (Buenos Aires, Argentina www.vicking.com.ar), was used for sample agitation.

2.2. Synthesis of Graphene oxide

GO was synthesized from natural graphite using a modified Hummers method, as reported in bibliography [39]. In brief, powered graphite was placed in a flask and treated with a mixture of concentrated H_2SO_4, P_2O_5, and $K_2S_2O_8$ for 6 h at 80 °C. After cooling and filtering, 1 g of this processed graphite was added to 23 mL H_2SO_4 with 0.5 g of $NaNO_3$ at a temperature below 40 °C and

stirred for 1 h. Three grams of $KMnO_4$ was added slowly, maintaining the temperature below 10 °C for 1 h and then heating to 38 °C holding for 0.5 h. Then 6 mL distilled water and 15 mL H_2O_2 were added to terminate the reaction. The resulting solution was washed with 40 mL HCl, centrifuged, and dried to give a brown solid. After exfoliation by ultrasonication in water for 30 min, a stable 0.1 % GO dispersion was obtained and used for ALIQUAT 336-GO preparation.

2.3. Preparation of the loaded GO

Under the optimized adsorption conditions previously published [39], the anion-exchanger extractant was loaded on the ground GO. A 5 mg GO mass was shaken overnight with 40 mL of 5% ALIQUAT 336 solution in methanol at room temperature. The GO were then filtered, washed with distilled water, and dried in an oven at 110 ºC.

2.4. *Sample pre-treatment*

The wines were purchased in local supermarkets and were selected based on a cost criterion: their cost was within 5 to 10 dolar/liter, which represents the most consumed wine brands in Argentine. The selected red wines were from the crop year of 2009-2017, which was the last crop year before this study began. The wines were all bottled in glass containers (1 L capacity) and cork sealed.

The wines were digested as follows: 8 mL of wine were placed in a 100 mL PTFE reactor and after that, 2 mL of concentrated nitric acid and 2 mL of hydrogen peroxide were added. Then the samples were digested applying different microwave powers, i.e. MW power was held at 250W (5 min.), 250W (5 min.), 500W (5 min.), 500W (5 min.). The vessels were then removed from the oven and cooled at 20 °C, after they were cooled and opened. After evaluation, the best adsorption conditions were achieved at a pH value of 8, which was selected for further experiments.

2.5. Batch adsorption experiment

A series of standards or sample solutions containing Cr(VI) were transferred into 25 mL beakers and the pH value was adjusted to the desired value with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH

solutions. The volume was made up to 10 mL with ultrapure water and 1 mg of ALIQUAT 336-GO was added. This mixture was then placed in a shaker for 20 min to facilitate adsorption of the metal ions onto the sorbent.

2.6. Preparation of the thin film

Membrane filter papers were Millipore of 0.45 µm pore size. Different amounts (1,3, 5, 10, 15, and 20 mg) of the loaded ALIQUAT 336-GO containing the preconcentrated Cr(VI) were used to prepare the films in order to determine the critical thickness of the film. The filtrations were performed in a filtration apparatus equipped with a vacuum pump [40].

A series of aqueous properly diluted Cr solutions were preconcentrated. This was done on the ALIQUAT 336-GO by the method described above. The measuring X-ray parameters were 66.23 2θ for Cr; Rh tube, 50 kV 50 mA, LiF (200) Crystal; 75-25 window width, counting time for peak and background 100 sec; gas proportional-scintillation counter in tandem.

3. Result and discussion

3.1. Study of retention of chromium on graphene and graphene oxide

To optimize the experimental parameters of the preconcentration system, the response of graphene modified with ALIQUAT 336 with and without prior oxidation was evaluated. With this aim, a Cr(VI) standard solution from 0.1 to 0.5 ppm was preconcentrated and applied to the procedure described above. Thus, we replicated of the experiment averaging the values obtained as shown in Figure 1, a better response was obtained using graphene with prior oxidation.

3.2. Effect of shaking time on sorption

The shaking time is an important factor in determining the possibility of application of ALIQUAT 336-GO to extraction of metal ions. In this work, considering the percentage extraction of Cr(VI) on ALIQUAT 336-GO, different shaking times (ranging from 1 to 60 min) were studied. This

effect on the adsorption of 1.0 mg L^{-1} of Cr(VI) on to ALIQUAT 336-GO as shown in Figure 2, which indicated that more than 95% Cr(VI) was extracted within 5 min.

3.3. Effect of pH on the retention

In order to evaluate the effect of pH, 10 mL solutions containing 1 mg L^{-1} of Cr(VI) were adjusted to different pH values with sodium hydroxide or hydrochloric acid. The range of pH studied was broad, of acid values, pH = 1 at alkaline values like pH = 12. They were mechanically shaken with 1 mg portions of ALIQUAT 336-GO for 10 min. Then, the ALIQUAT 336- GO was filtered, washed with distilled water, and later the Kα lines of the analyte were measured by the X-ray Fluorescence Spectrometer. As shown in Figure 3, the XRF highest intensites of Cr Kα as function of pH were obtained between pH 6 and 9; therefore, pH 8 was selected for further experiments.

3.4. Sample volume and preconcentration factor

Because of the importance of obtaining high preconcentration factors, the effect of sample volume on recovery of Cr on the solid phase was also examined. In order to evaluate this effect, solutions containing 1 mg L^{-1} of Cr(VI) were adjusted to different volume. The results are given in Fig. 4. Cr(VI) ions were quantitatively (>95%) recovered within the volume range 5–100 mL. Therefore, 10– 100 mL sample solution was adopted as volume range for separation and preconcentration of Cr.

3.5. Determination of the maximum capacity of retention of the ALIQUAT 336-GO

Solutions containing different concentrations of Cr(VI) from 0.1 to 0.5 ppm, were adjusted to pH 8, shaken and filtered to determine the quantity of analyte that saturated the ALIQUAT 336-GO material. In Figure 5, the XRF intensity of Cr Kα as function of the Cr(VI) concentration is shown. For low Cr(VI) amounts, the concentration was proportional to the Cr Kα intensity. The curve was linear up to 1 mg L^{-1} of Cr(VI) and became constant at higher Cr concentrations. The total capacity retention was 1000 mg of Cr(VI) per gram of sorbent material. The amount of Cr(VI) not retained by the

ALIQUAT 336-GO was determined by inductively coupled plasma optical emission spectrometric analysis of the filtrate. The amount retained was always greater than 95%.

3.6. Analytical performance

The enrichment factor is defined as EF = [QT/ QM]/[QT_0/QM_0] [43], where: QT_0 and QT are the analyte quantities before and after the preconcentration, respectively; and QM_0, QM are the quantities of the matrix before and after the enrichment, respectively. The enrichment factor was calculated considering that the thin film obtained from the 10 mL solution of 1000 µg L^{-1} Cr(VI) had a final thickness of 0.04 mm and a final diameter of 16.7 mm, the volume deposited on the pellet was 0.0088 cm^3. The preconcentration factor obtained was 10^4 fold, which represented a highly satisfactory value for trace analysis by XRF.

One of the most important features of the use of a preconcentration method is the improvement of the detection limits. A detection limit of 0.35 µg L^{-1} was obtained for wine samples, this was calculated as $(3/m)(I_b/t)^{1/2}$, where *m=slope of the calibration curve* , I_b=*background intensity (counts/*s^{-1}*) and t=counting time (s).*

Various preconcentration procedures for the determination of chromium have been reported, Table 1 shows a comparison among the most influential ones. The precision, expressed as relative standard deviation, for ten replicate determinations at 1 mg L^{-1} Hg(II) level was 4.0%.

3.7. Recovery study

We have no standard reference materials with a certified content of chromium. In this case, a recovery study can be considered as a validation alternative but is not a complete validation, is only a part [44], this procedure was applied to the developed methodology. Thus, we collected six samples with a volume of 100 mL of red wines were from the crop year of 2009-2017 and divided in ten aliquots of 10 mL each one. The methodology described above was applied to six portions for each sample and the average quantity of chromium obtained was taken as a base value. Then, increasing

quantities of chromium were added to the other aliquots of sample, after that chromium was determined by the same method. The results are shown in Table 2. The other elements present in the sample do not showed spectral interferences in the determination. A full scan using the Cr Kα line was obtained and no spectral interferences were observed (Figure 6).

5. Conclusions

The wine consumption in this country is of considerable. These data indicate that wine can have a significant contribution to the dietary intake of chromium. The normal range for chromium concentrations in wine from 2 to 90 μg L^{-1} [15]. A measure of the human absorption of this element after wine ingestion is also necessary to assess potential health effects by stainless steel or after bottling by chromium oxides used for pigmentation of the bottle during the aging process.

Although the preconcentration procedure of this methodology was similar to the method developed in our research group where we employed activated carbon on nanotubes as adsorbent for solid-phase extraction coupled XRF [36]; furthermore, graphene-based material has been used successfully for preconcentration of trace level metal ions, from water samples as well as complex biological matrices such as milk, fish, vegetables and wine. Graphene oxide provides high hydrophilic affinity due to rich functional groups. These advantages are the main factors in adsorption process as they contributed towards graphene-based material to become a suitable adsorbent candidate in analytical chemistry.

The preconcentration methodology here presented enabled the determination of Cr(VI) at μg L^{-1} levels in red wine. In addition to the 10^{-4} fold EF achieved, the analyte elution step was not required; these aspects allowed a substantial improvement of chromium detection limit by XRF, moreover the ALIQUAT 336-GO based procedure is superior to those reported chromium separation–preconcentration methods in term of selectivity, detection limit, pH range applicability, without the

need for organic solvent consumption, in addition the method described presents an adequate reproducibility and precision.

Acknowledgments

This work was supported by Universidad Nacional de San Luis (UNSL), Instituto de Química de San Luis (INQUISAL), Facultad de Química, Bioquímica y Farmacia (FQBF), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT-FONCYT).

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Figure captions

Figure 1. Retention of Cr(VI) on graphene modified with ALIQUAT 336 with and without prior oxidation.

Figure 2. Effect of shaking time on the adsorption of 1.0 mg L^{-1} of Cr(VI) on to ALIQUAT 336-GO.

Figure 3. Effect of pH on adsorption of 1.0 mg L^{-1} Cr(VI) on ALIQUAT 336-GO.

Figure 4. Effect the sample volume on SPE recovery of 1.0 mg L^{-1} Cr(VI).

Figure 5. Retention capacity of Cr(VI) on the ALIQUAT 336-GO

Figure 6. Scanning XRF spectrum of a red wine sample.

Figure 1

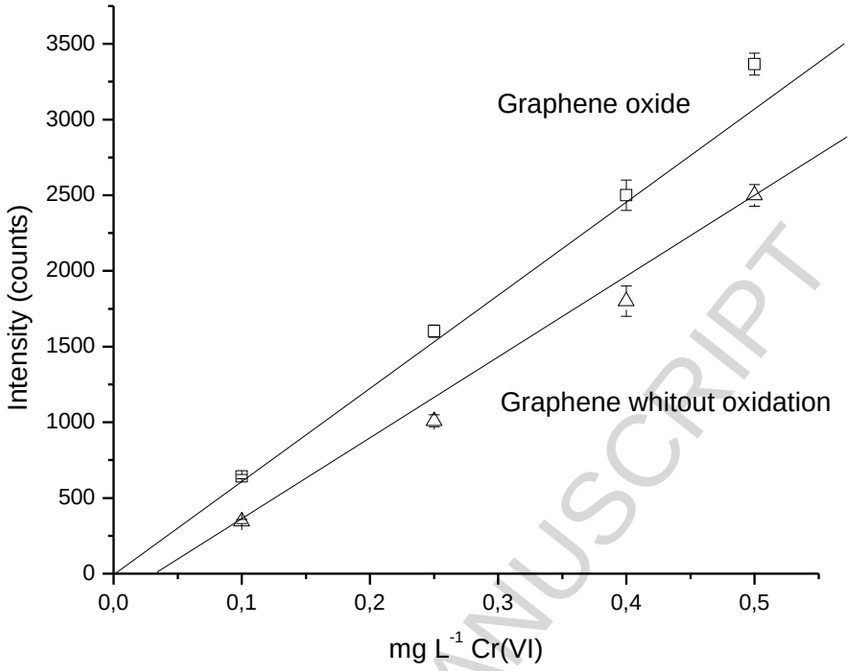

Figure 2

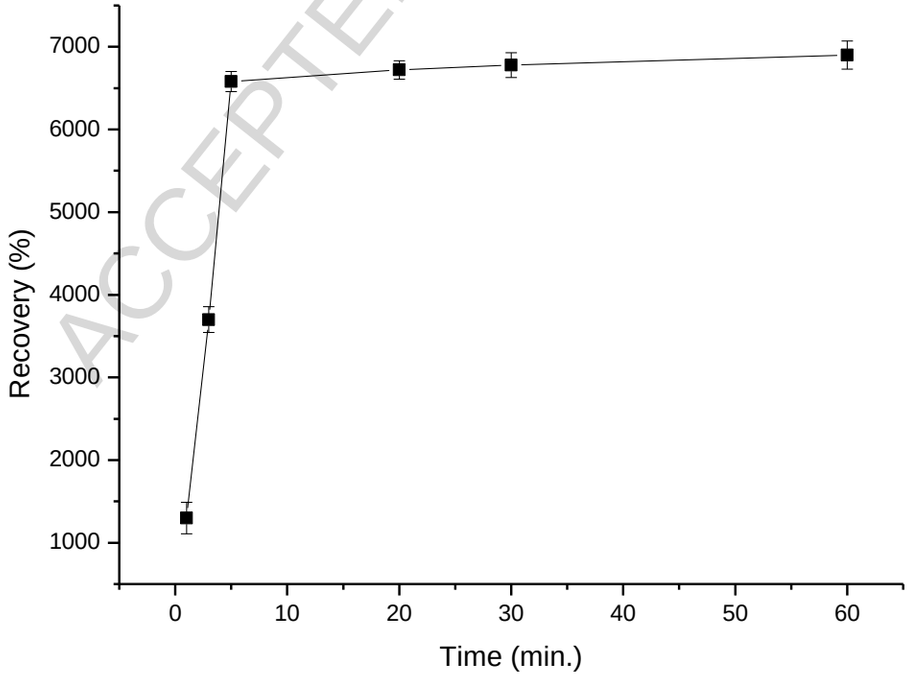

Figure 3

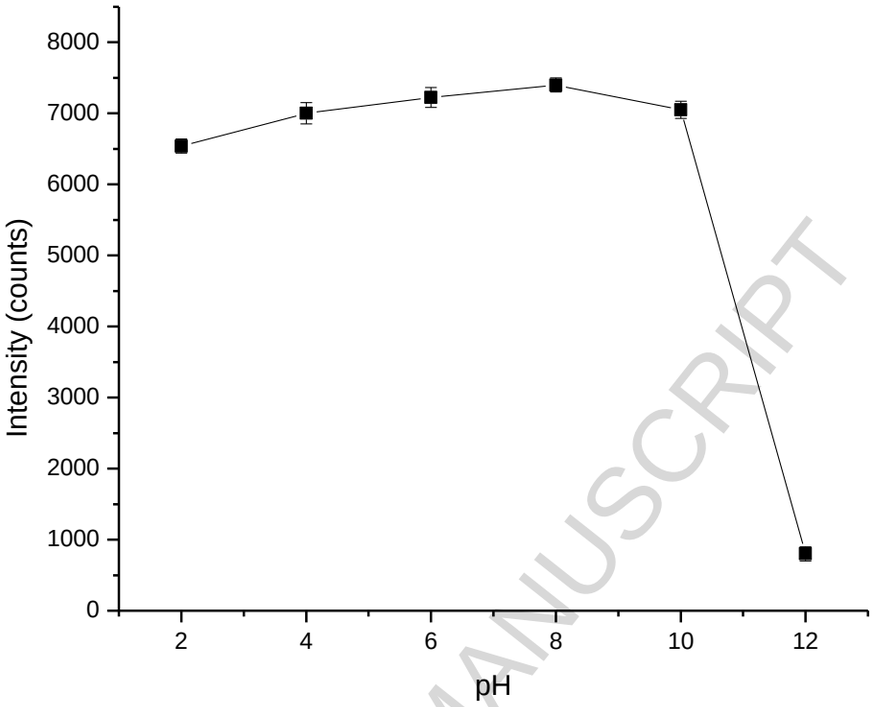

Figure 4

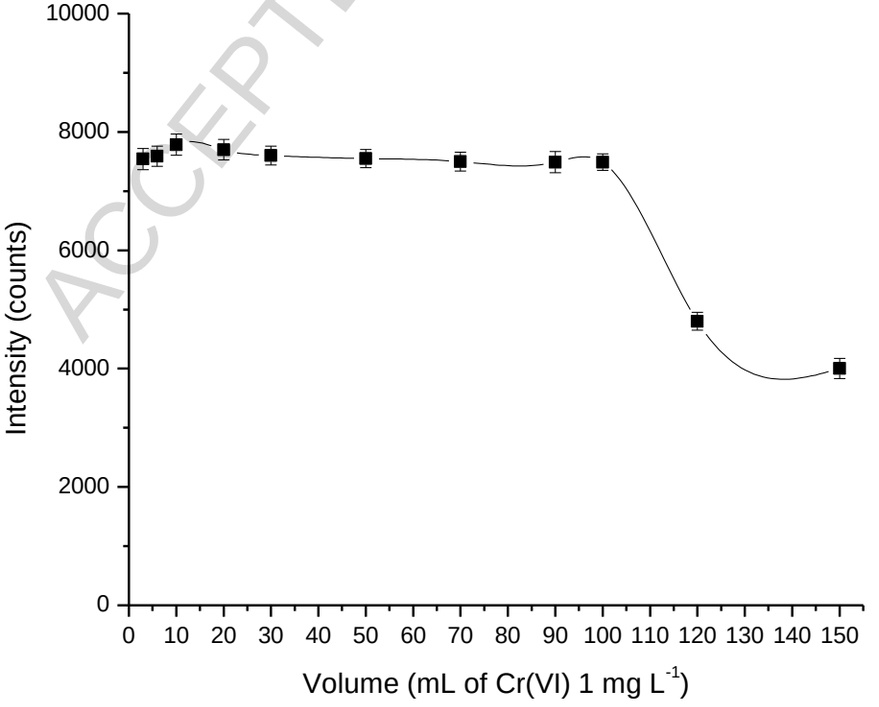

Figure 5

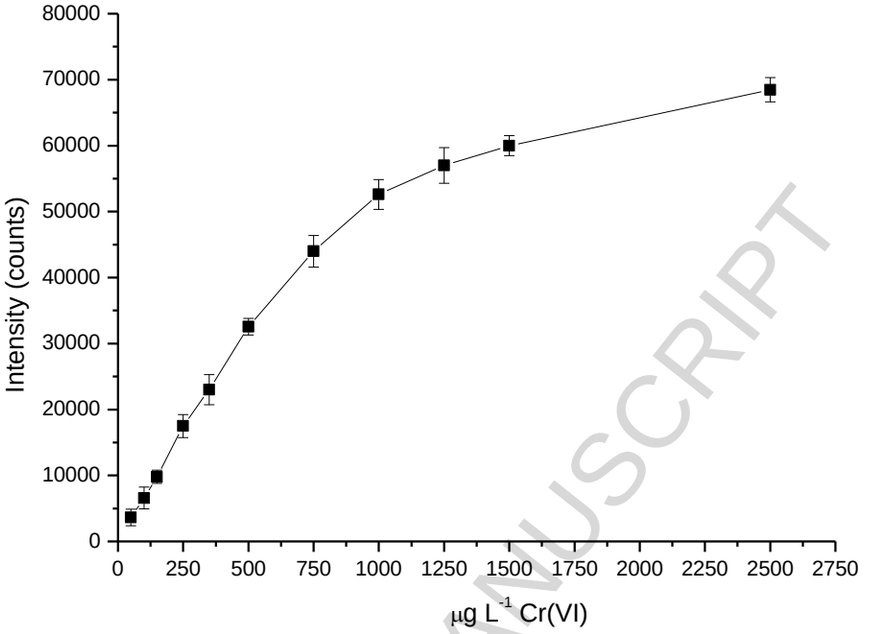

Figure 6

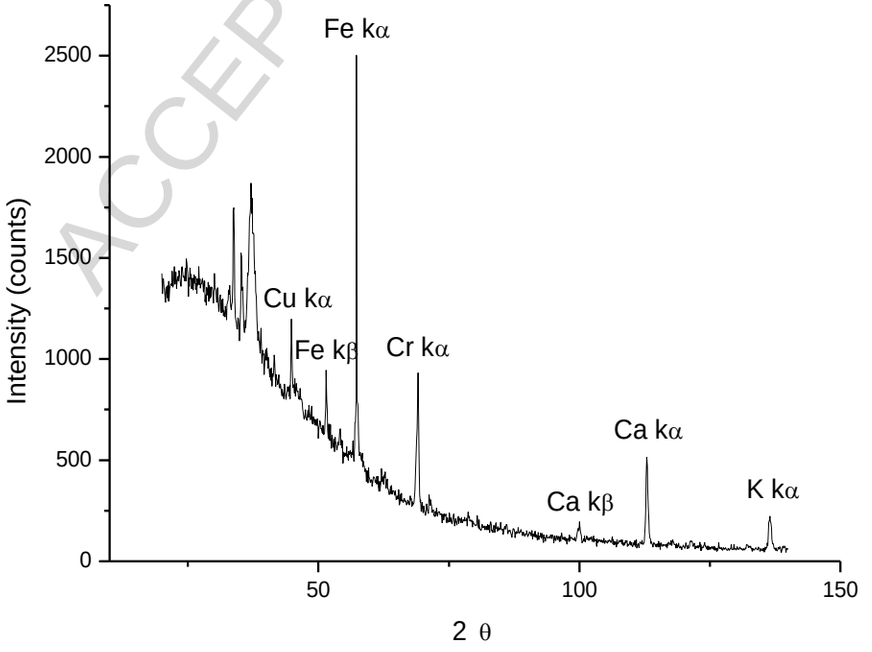

Table 1

Procedures for preconcentration and determination of chromium.

Detection limit ($\mu g\ L^{-1}$)	**Enrichment factor**	**Sample volume (mL)**	**Technique**	**References**
0.35	10^4	10	XRF	This work
0,5	10^3	10	XRF	36
0.003	35	10	ETAAS	21
2.0–6.0	23–61	18	FAAS	45
0.002–0.005	100	100	ETAAS	46

Table 2

Concentrations of Cr (VI) in red wine for human consumption (95% confidence level; $n = 6$)

Base ($\mu g\ L^{-1}$)	Cr (VI) Added ($\mu g\ L^{-1}$)	Cr (VI) Found ($\mu g\ L^{-1}$)	Recovery (%)[a]
5.0	0.0	5.0±0.3	-
5.0	100.0	105±6.0	100
5.0	250.0	251±10.0	98.4
5.0	500.0	504±15.0	99.8
5.0	750.0	757±19.0	100.2
5.0	1000.0	1006±25.0	100.1

[a] [(Found - base)/added] x 100

Highlights

- This system of preconcentration enabled determination of the toxic species of ultra-trace of (Cr) in red wine samples at µgL-1 levels.
- The high EF obtained encouraged us to propose this preconcentration methodology as a worthy tool for trace analysis by XRF determination
- The determinations were made directly on the solid by XRF spectrometry, which had the advantage of eliminating the step of elution of the chromium retained..
- The procedure of graphene oxide based on higher than those reported Chromium preconcentration methods of separation in terms of selectivity, detection limit, without consumption of organic solvents, and the reliability and accuracy of the method described.